CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

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PHYSICAL METALLURGY DIVISION

INTERNAL REPORT PM-R-68-12

DISPERSION STRENGTHENING ZIRCONIUM

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June 10, 1968

90-04653/

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ABSTRACT

In this investigation, it was established that thorium oxide (ThO_2) when added to molten zirconium dissolved and, on cooling, precipitated as a dispersed phase at the boundaries of alpha platelets. Thorium oxide was shown to be soluble in solid zirconium at temperatures of 900°C and above.

By selective heat treatment, ThO_2 particles small enough to cause dispersion strengthening (0.03 micron) were obtained, however the distance between the boundaries of alpha platelets, on which the ThO_2 precipitated, was such that particle spacing was not of the order necessary for blocking of dislocation movements.

Ultimate tensile strengths as high as 27 kpsi at 650°C

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are believed to be due to the ThO_2 particles interfering with recrystallization and grain growth at the testing temperature.

INTRODUCTION

An investigation is being carried out in these laboratories to determine the possibility of improving the high-temperature properties of zirconium through dispersion strengthening by addition of refractory compounds to the molten metal. To strengthen zirconium by this method it is necessary for a thermodynamically stable refractory compound to dissolve in molten zirconium, then, on cooling, to precipitate as a fine dispersion of the original additive or of some stable quasi-refractory formed by reaction with the zirconium.

Because of its high stability, thorium oxide (ThO_2) was selected to test the above proposition. The high neutron capture cross-section and fertile nature of thorium render it unacceptable in alloys for reactor use, but the principles established will serve as a basis for future work on other zirconium-refractory and metal-refractory systems.

EXPERIMENTAL PROCEDURE

Preparation of Alloys

The materials used in preparing Zircaloy-2 and the experimental alloys are listed in Table 1. The reactor grade zirconium sponge contained 1100 ppm oxygen. The ThO_2 was in powder form.

The experimental alloys prepared for this investigation are listed in Tables 2 and 3 (zirconium and Zircaloy-2 are also included). These alloys were prepared in a laboratory-size tungsten-arc furnace. Melting and alloying were carried out by striking an arc between the tungsten electrode and the charge contained in a water-cooled copper hearth. An atmosphere of argon at a pressure of 350 mm mercury was maintained during melting.

The zirconium sponge was consolidated by melting into dense material in which a cavity was drilled to contain the ThO_2 powder. The powder was heated to 800°C for 1 hr, then cooled in vacuum before being added to the zirconium. Each charge weighed approximately 75 grams and was remelted at least 4 times to ensure homogeneity. The final melt was made in a hearth that produced a cigar-shaped ingot.

The Zr-0.64% Th, Zr-0.34% ZrO_2 and Zr-0.64% Th-0.34% ZrO_2 alloys were prepared to determine the effect of thorium and oxygen separately and together, arising from any possible decomposition of the ThO_2. The 0.64% Th and the oxygen in 0.34% ZrO_2 are equivalent to the thorium and oxygen contained in 0.7% ThO_2.

Swaging and Heat Treatment

Some arc-melted ingots were swaged at 500°C to 0.35 in. diameter rod. All heat treatments were carried out in vacuum or in a non-oxidizing atmosphere.

Tensile Testing

Tensile tests were carried out at 650°C in a vacuum of 5×10^{-5} mm mercury using an Instron universal testing machine. The test specimens had a 1 in. gauge length and a 0.16 in. gauge diameter. Each specimen was held at temperature for 1 hr before testing. Duplicate tests were carried out on each alloy.

The test specimens were machined from arc-melted ingots, as-swaged rods, and swaged and heat treated rods. Alloy compositions and metallurgical conditions of specimens that were tensile tested are listed in Table 3.

Oxygen Analysis

Specimens of arc-melted alloys containing 0.7% ThO_2, 0.64% Th, 0.34% ZrO_2 and 0.64% Th plus 0.34% ZrO_2 were analysed for oxygen by the vacuum fusion method.

Metallography

The specimens for microexamination were prepared by first rough polishing on silicon carbide abrasive paper to 600 grit, followed by polishing with 9 micron and 1/4 micron diamond paste on "Microcloth". The specimens were then chemically polished by swabbing with a solution containing 45 cc distilled water, 45 cc nitric acid and 8 to 10 cc hydrofluoric acid.

To investigate the dispersed phase present in Zr-ThO_2 alloys, specimens 1/4 in. thick were cut from ingots in the metallurgical conditions listed in Table 2.

X-Ray Diffraction Analysis

X-ray diffraction analysis was carried out on a GE diffractometer using CuK alpha radiation. The specimens were prepared for X-ray diffraction analysis in the same manner as described under "Metallography".

Specimens of the Zr-2.5% ThO_2 alloy that were heat treated at 800°C for 24 hr to coalesce the precipitate were analysed.

RESULTS

Examination of the Dispersed Phase

The photomicrographs in Figures 1 and 2 illustrate the microstructure of the Zr-0.7% Th and Zr-0.7% ThO_2 alloys after swaging at 500°C followed by heat treating at 700°C for 6 hr. A second phase is evident in the Zr-0.7% ThO_2 specimen but not in the Zr-0.7% Th specimen. There was not a sufficient amount of this phase in the Zr-0.7% ThO_2 alloy to permit identification by X-ray diffraction analysis but a similar phase present in the Zr-2.5% ThO_2 alloy was identified by X-ray analysis as ThO_2 after the alloy had been heat treated at 800°C for 24 hr to coalesce the phase (see Figure 3).

The photomicrograph and electron micrographs in Figures 4 to 9 show the effect of heat treatment on the size, distribution and solubility of the ThO_2 in a Zr-2.5% ThO_2 alloy. The photomicrograph in Figure 4 and electron micrograph in Figure 5 illustrate the structure of the as-arc-melted specimens and show the ThO_2 at the alpha-platelet boundaries. Heat treating at 900°C for 6 hr and water quenching produced an arrangement of the ThO_2 that was different from that observed in specimens heat treated at 800°C for 24 hr and water quenched. (Compare electron micrographs in Figures 3 and 6). In the microstructure of specimens heat treated at 950°C and shown in the electron micrograph in Figure 8, the smaller particles of ThO_2 are in the order of 0.03 micron while the ThO_2 particles in specimens heat treated in a vacuum furnace at 1400°C for 24 hr and furnace cooled are as large as 3 microns (Figure 9).

The electron micrograph in Figure 10 shows the structure of a Zr-2.5% ThO_2 alloy specimen after water quenching from the molten state. There is little evidence of any ThO_2 at the fine alpha-platelet boundaries. However, after ageing at 700°C for 6 hrs, ThO_2 particles precipitated out of solution, as is shown in the electron micrograph in Figure 11.

Tensile Tests

Table 3 lists the results of tensile tests carried out at 650°C on the experimental zirconium-refractory alloys in various metallurgical conditions.

All the alloys containing 2.5% or more ThO_2 had high temperature tensile strengths greater than Zircaloy-2 and no significant increase in strength was obtained by increasing the ThO_2 content from 2.5% to 7.0% or by heat treating the Zr-2.5% ThO_2 alloy at temperatures of 650°C and 950°C. However, after specimens of the Zr-0.7% ThO_2 alloy were swaged at 500°C and heat treated at 700°C for 6 hr, the ultimate tensile strength increased to 23.6 kpsi from 16.2 kpsi for as-arc-melted specimens. It can be seen that the tensile strengths of Zr-0.64% ThO_2, Zr-0.34% ZrO_2 and Zr-0.64% Th-0.34% ZrO_2 are less than half that of Zr-0.7% ThO_2 swaged and heat treated, and substantially below that of Zr-0.7% ThO_2 as-arc-melted.

Oxygen Analysis

The oxygen analysis results given in Table 4 show that addition of ZrO_2 to zirconium and to Zr-0.64% Th was effective in increasing the oxygen content to the same as that of the Zr-0.7% ThO_2 alloy.

DISCUSSION

Considerable precipitate was observed at the alpha-platelet boundaries of specimens of the Zr-2.5% ThO_2 alloy in various metallurgical conditions as shown by the photomicrograph and electron micrographs in Figures 4 to 9. From the electron micrographs in Figures 6 and 7 it appears that at 900°C and 950°C the ThO_2 dissolved in the zirconium and precipitated at

the alpha-platelet boundaries during water quenching. The electron micrograph in Figure 3 shows that at 800°C the ThO_2 was sufficiently soluble in zirconium to enable coalescence to occur. X-ray diffraction analysis of the latter specimen identified the precipitate as ThO_2, thus proving that this compound persisted in zirconium after melting and heat treating.

On water quenching the specimens direct from levitation melting very little precipitate was observed in their microstructure (see Figure 10), indicating that ThO_2 was soluble in molten zirconium and was substantially retained in solution on quenching. Ageing these specimens resulted in the appearance of a small amount of precipitate, as shown in Figure 11. The reason why the precipitate was retained in solution on quenching from the molten state and not retained in solution on quenching from 900°C or 950°C is not clear. A possible explanation is that the quench from the molten state was the more efficient. In the 900°C and 950°C heat treatments the specimens were wrapped in tantalum foil and sealed under vacuum in a quartz capsule; quenching was accomplished by breaking the capsule under water. It is possible that the cooling rate was higher when the levitation melted specimens were quenched by dropping them directly into water. The comparatively small amount of precipitate occurring in the aged specimens after quenching from the molten state might have been due to insufficient ageing. These points will be checked in future work.

Refinement of the ThO_2 particles to 0.03 micron by heat treating at 950°C (Figure 8) did not produce a corresponding improvement in tensile properties (Table 3). This lack of response of the tensile properties to refinement of the dispersed phase may have been due to insufficient reduction in the size of the alpha platelets. As a result, the spacing of the ThO_2 particles on the platelet boundaries was not reduced to the order of magnitude required for blocking of dislocation movement.

This work has demonstrated that arc-melted Zr-ThO_2 alloys can be heat treated to produce precipitated ThO_2 particles of the size necessary for dispersion strengthening but the required interparticle spacing has not been obtained.

However, as the results in Table 3 demonstrate, all the Zr-ThO_2 alloys (except Zr-0.7% ThO_2 as-arc-melted) have elevated temperature tensile strengths significantly higher than zirconium or Zircaloy-2. The possibility of this strengthening being due to the solution in zirconium of either elemental thorium or oxygen has been disproved by the fact that the alloys containing percentages of thorium and oxygen equal to the amounts of these elements in the Zr-0.7% ThO_2 alloy had inferior high temperature tensile properties to the latter when all were hot swaged and heat treated at 700°C for 6 hr (Table 3).

It would then appear that in the Zr-ThO_2 alloys examined, the high temperature strength was due to the ThO_2 particles interfering with recrystallization and grain growth at the testing temperature. This is supported by the fact that hot swaged Zr-0.7% ThO_2 specimens had considerably higher tensile strength than the as-arc-melted specimens even after annealing at 700°C for 6 hr.

The Zr-0.64% Th-0.34% ZrO_2 alloy was examined to determine if the thorium and oxygen added separately to the zirconium had combined to form a precipitate similar to that obtained with the Zr-0.7% ThO_2 alloy. The microstructure did not show any evidence of particles comparable to those found in the Zr-0.7% ThO_2 alloy (Figure 2).

CONCLUSIONS

1. An alloy with high temperature (650°C) tensile strength 1-1/2 times that of Zircaloy-2 can be produced by addition of ThO_2 to zirconium.

2. The dispersed phase observed in arc-melted Zr-ThO_2 alloys is ThO_2.

3. ThO_2 is soluble in molten zirconium.

4. In solid zirconium, at temperatures of 900°C and above, the ThO_2 dissolves then, on cooling, precipitates at the boundaries of alpha platelets.

5. By selected heat treatment, ThO_2 particles as small as 0.03 micron can be produced.

6. The ThO_2 particles in the Zr-ThO_2 alloys were not uniformly distributed but were mainly at the alpha-platelet boundaries. Since the distance between the platelet boundaries is not of the order of a fraction of a micron, the interparticle spacing of the ThO_2 particles is too great for dispersion strengthening.

7. No significant increase in the high temperature strength was obtained by increasing the ThO_2 content from 2.5% to 7.0%.

8. The high temperature strength of Zr-ThO_2 alloys is not due to solution in zirconium of thorium or oxygen arising from the decomposition of ThO_2.

FUTURE WORK

The experience gained in this work will be applied to other metal-refractory alloy systems.

Investigations in progress at the writing of this report show that in Zr-Ce_2O_3.2 ZrO_2, Zr-Y_2O_3 and Ti-ThO_2 alloys the refractory dissolves in the molten metal and precipitates out of solution on cooling. A dispersed phase has also been observed in arc-melted Zr-La_2O_3, Zr-CeO_2, Zr-$MgZrO_4$ and Zr-Ce_2O_3 alloys.

Effect of cold and hot work on the interparticle spacing and high temperature properties of metal-refractory alloys will also be investigated.

ACKNOWLEDGEMENTS

The authors wish to thank Miss Joyce Ng-Yelim for assistance in obtaining the electron micrographs and Dr. C. M. Mitchell for X-ray diffraction analysis.

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TABLE 1

Materials Used to Prepare Experimental Alloys

Material	Purity	Source
Zirconium Sponge	Reactor Grade	Carborundum Metals Co.
Thorium	98%	Dominion Magnesium Ltd.
Thorium Oxide(ThO_2)	Purified	Anachemia Chemicals Ltd.
Zirconium Oxide(ZrO_2)	99.8%	Titanium Zirconium Co.
Tin	99.98%	Hewitt Metals Corp.
Chromium	99.9%	Shieldalloy Corp.
Nickel	Electrolytic	International Nickel Co.
Iron	99.9%	A. D. McKay Inc.

TABLE 2

Heat Treatment of Zr-Th and Zr-ThO_2 Alloys for Observations of the Dispersed Phase

Melt Ident.	Nominal Composition	Heat Treatment
IV	Zr-0.7% Th	Swaged 500°C, HT 700°C 6 hr, WQ
KG	Zr-0.7% ThO_2	Swaged 500°C, HT 700°C 6 hr, WQ
PT	Zr-2.5% ThO_2	As-Arc-Melted
PX	Zr-2.5% ThO_2	800°C 24 hr, WQ
PT	Zr-2.5% ThO_2	900°C 6 hr, WQ
PT	Zr-2.5% ThO_2	950°C 6 hr, WQ
PT	Zr-2.5% ThO_2	1400°C 24 hr, Furnace Cooled
PX	Zr-2.5% ThO_2	Levitation Melted, WQ
PX	Zr-2.5% ThO_2	Levitation Melted, WQ Aged 700°C 6 hr, WQ

WQ - Water Quenched.

TABLE 3

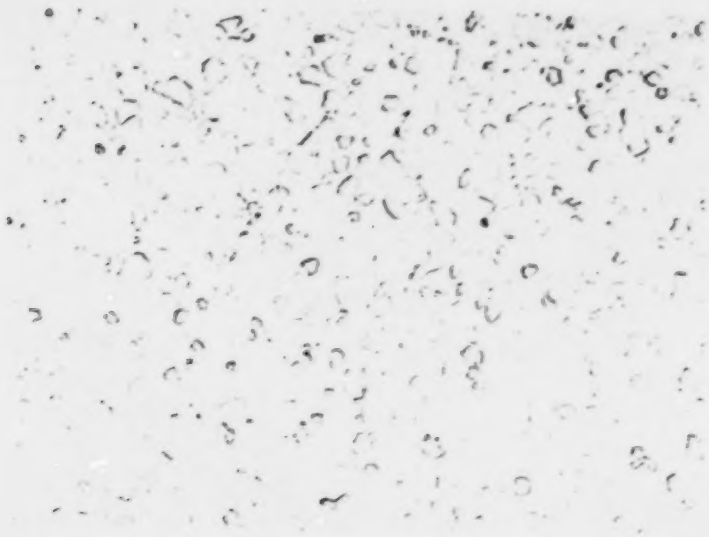
Tensile Properties of Zirconium and Zirconium Alloys at 650°C

Melt Ident.	Nominal Composition	Condition	UTS kpsi	.2% YS kpsi	% El on 1 in.
	Zr	As-Arc-Melted	11.2	7.5	44
	Zircaloy-2	As-Arc-Melted	17.6	11.9	42
NT	Zr-0.64% Th	Swaged 500°C,HT 700°C 6 hr,WQ	9.5	4.7	63
NU	Zr-0.34% ZrO_2	Swaged 500°C,HT 700°C 6 hr,WQ	10.0	5.6	59
NV	Zr-0.64% Th-0.34% ZrO_2	Swaged 500 C,HT 700°C 6 hr,WQ	9.7	4.0	66
KG	Zr-0.7% ThO_2	Swaged 500 C,HT 700°C 6 hr,WQ	23.6	14.7	48
RQ	Zr-0.7% ThO_2	As-Arc-Melted	16.2	10.9	36
RR	Zr-2.5% ThO_2	As-Arc-Melted	23.7	16.8	27
PF	Zr-3.5% ThO_2	As-Arc-Melted	27.0	17.3	35
PG	Zr-5.0% ThO_2	As-Arc-Melted	26.6	17.7	26
PH	Zr-7.0% ThO_2	As-Arc-Melted	25.5	16.3	20
OQ	Zr-2.5% ThO_2	HT 650°C 6 hr,WQ	26.1	17.5	22
QN	Zr-2.5% ThO_2	HT 950°C 6 hr,WQ	23.7	16.5	27

TABLE 4

Oxygen Content of Samples Swaged at 500°C
Then Heat Treated at 700°C for 6 Hours

Melt Ident.	Nominal Composition	Oxygen Content (Wt %)
KG	Zr-0.7% ThO_2	0.20
NT	Zr-0.64% Th	0.11
NU	Zr-0.34% ZrO_2	0.20
NV	Zr-0.64% Th-0.34% ZrO_2	0.20



X150

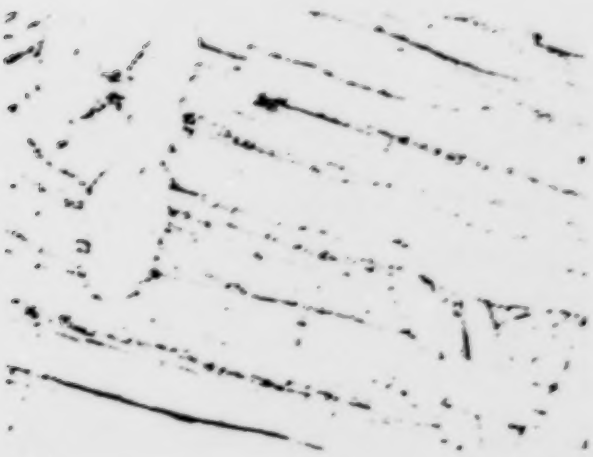
Figure 1. Zr-0.7% Th, Melt IV, Swaged 500°C, HT 700°C 6 hr, WQ. Chemical Polish.

X150

Figure 2. Zr-0.7% ThO_2, Melt KG. Swaged 500°C, HT 700°C 6 hr, WQ. Chemical Polish.

X5,000

Figure 3. Zr-2.5% ThO_2, Melt PX, HT 800°C, 6 hr, WQ, Chemical Polish.



X1,000

Figure 4. Zr-2.5% ThO_2, Melt PT, As-Arc-Melted, Chemical Polish.

X5,000

Figure 5. Zr-2.5% ThO_2, Melt PT. As-Arc-Melted. Chemical Polish.

X5,000

Figure 6. Zr-2.5% ThO_2, Melt PT. HT 900°C, 6 hr, WQ. Chemical Polish.

X5,000

Figure 7. Zr-2.5% ThO_2, Melt PT. HT 950°C, 6 hr, WQ. Chemical Polish.

X30,000

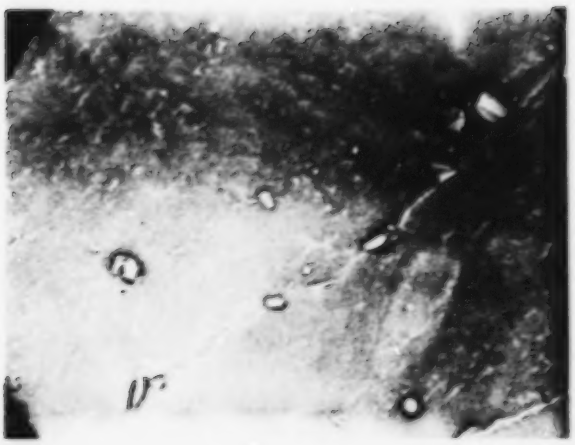
Figure 8. Zr-2.5% ThO_2, Melt PT. HT 950°C, 6 hr, WQ. Chemical Polish.

X5,000

Figure 9. Zr-2.5% ThO_2, Melt PT. HT 1400°C, 24 hr, Furnace Cooled. Chemical Polish.

X10,000

Figure 10. Zr-2.5% ThO_2, Melt PX. Levitation Melted, WQ. Chemical Polish.



X5,000

Figure 11 . Zr-2.5% ThO_2, Melt PX. Levitation Melted, WQ. Aged 700°C, 6 hr, WQ. Chemical Polish.